

# THE LIPID HANDBOOK

*edited by*

**FRANK D. GUNSTONE**

*University of St Andrews, Scotland*

**JOHN L. HARWOOD**

*University College, Cardiff, Wales*

**FRED B. PADLEY**

*Unilever Research, Sharnbrook, England*

SCIENTIFIC & TECHNICAL  
INFORMATION CENTER

DEC 13 1993

PATENT & TRADEMARK OFFICE

London New York

Chapman and Hall

A.U. 180/BTECH REF

QP

751

L547

1986

First published in 1986 by  
Chapman and Hall Ltd,  
11 New Fetter Lane, London EC4P 4EE  
Published in the USA by  
Chapman and Hall  
29 West 35th Street, New York NY 10001

© 1986 Chapman and Hall Ltd  
Printed in Great Britain at  
The University Press, Cambridge

ISBN 0 412 24480 2

All rights reserved. No part of this book may be reprinted,  
or reproduced or utilized in any form or by any electronic, mechanical  
or other means, now known or hereafter invented, including  
photocopying and recording, or in any information storage and  
retrieval system, without permission in writing from the publisher.

---

British Library Cataloguing in Publication Data

---

The Lipid handbook.

1. Lipids

I. Gunstone, F.D.

II. Harwood, John L.

III. Padley, F.B.

547.7'7 QP751

ISBN 0-412-24480-2

---

---

Library of Congress Cataloging-in-Publication Data

---

Main entry under title:

The Lipid handbook.

Includes bibliographies and index.

1. Lipids—Handbooks, manuals, etc.

I. Gunstone, F.D.

II. Harwood, John L.

III. Padley, F.B. (Fred B.), 1936—

[DNLM: 1. Lipids.

QU 85 L7632]

QP751.L547 1986

574.19'247

85-24306

ISBN 0-412-24480-2

---

## 5.8 Surfactants and emulsifiers

The consumption of industrially manufactured food products is increasing in modern society. Consumers are changing their way of purchasing food items from a daily to a weekly habit, and therefore a longer shelf life of distributed foods is needed. To produce food products with the quality and shelf life required by the consumer, the food industry utilizes surface-active lipids (surfactants, emulsifiers), which are chemical derivatives of natural edible fats and oils, or fatty acids.

Surfactants are amphiphilic lipids, having both hydrophilic and lipophilic properties which can be influenced by varying their chemical composition. They play an important role in many foods, not only in emulsions to give stability or control viscosity (flocculation), but also as complexing agents in starch-containing products or crystal modifiers in fats.

This section reviews food-grade surfactants, their chemical and physical characteristics, application and functions in food products and legal aspects.

Surfactants are partial esters of fatty acids with chain lengths from  $C_{12}$  to  $C_{22}$  and polyvalent alcohols like glycerol, propylene glycol, sorbitol/sorbitan and sucrose, or organic hydroxy acids like lactic acid. Furthermore the partial esters, e.g. monoglycerides, may be either esterified with organic acids such as acetic acid, lactic acid, diacetyl-tartaric acid, succinic acid or citric acid, or reacted with ethylene oxide forming a wide range of esters with big variations in properties and functions. The most commonly used types of emulsifiers are listed in Table 5.6.

Soybean phosphatides, generally called lecithin, are included in this section as they are naturally occurring emulsifiers often used in combination with synthetically produced emulsifiers.

### 5.8.1 Monoglycerides (monoacylglycerols)

Monoglycerides of saturated and unsaturated fatty acids are by far the most commonly used food surfactants accounting for over 70% of the total world use. On an industrial scale monoglycerides are normally produced by interesterification of fats or oils with glycerol (also called glycerolysis, Section 10.12), by reacting the components at 180–230 °C under alkaline catalysis.

The chemistry of polyol surfactants is reviewed by Benson (1967), and inter esterification processes are described by Sonntag (1982). Synthetic procedures for monoglycerides are dealt with in Chapter 7.

Monoglycerides produced by high-vacuum thin-film molecular distillation contain approximately 95% monoglyceride, 3% diglyceride, <1.0% free glycerol and <1.0% free fatty acid. Of the 95% total monoglycerides in the fresh distillate only 84–88% is 1-monoglyceride, the balance being 2-monoglyceride. When the distilled monoglyceride is cooled, either by spray-crystallization (bead or powder form) or by plastification in a heat exchanger (votator type), most of the 2-monoglyceride is converted by acyl migration into 1-monoglyceride resulting in a 1-monoglyceride content in equilibrated distilled monoglyceride of at least 90% and often 93% or above.

The 1-monoester content is usually determined by a standard periodic acid titration method (A.O.C.S. Cd. 11–57) and total monoglyceride content can be determined quantitatively by modern gas liquid chromatography methods (Søe, 1983).

Mono-diglyceride mixtures as well as distilled monoglycerides are polymorphic like triglycerides. Mono-diglycerides crystallize from the melt in an  $\alpha$ -form and on further cooling transform into a sub- $\alpha$ -form (also called  $\beta'_2$ ) at a temperature 20–25 °C below the melting point of the  $\alpha$ -form. The  $\alpha$ -form is metastable and will transform into a higher-melting stable  $\beta$ -crystal form. The crystallography of monoglycerides is described in detail in Section 8.7.

#### (a) Lyotropic mesomorphism

Monoglycerides are completely soluble in fats and oils and dispersible in water under certain conditions. Distilled monoglycerides form mesomorphic phases in water depending on temperature, concentration, fatty acid chain length and degree of unsaturation.

Reviews of the phase behaviour in water of commercial distilled monoglycerides and some of their derivatives can be found in the literature (Krog, 1975; Krog and Birk Lauridsen, 1976). The lamellar mesophase is considered an important physical form for various applications in foods (aeration, foam and emulsion stability, starch complexing ability). It consists of bimolecular layers of monoglycerides (preferably saturated) oriented with the polar groups towards layers of water which separate the lipid bilayers. The continuous water layers can be up to 1000 Å thick in lamellar phases of saturated ( $C_{16}/C_{18}$ ) distilled monoglyceride with high water contents ( $\geq 90\%$ ). Such phases are translucent low-viscous liquids. The salt concentration in the water phase

must be low ( $<0.05\%$ ), and the minor quantity of free fatty acids ( $<1\%$ ) should be at least partially neutralized in order to obtain a complete swelling proportional to the water content (Krog and Borup, 1973).

Figure 5.9 shows binary phase diagrams of distilled monoglycerides in water. The optimal temperature range for making lamellar dispersions of saturated, distilled monoglycerides is  $60\text{--}65^\circ\text{C}$ . Such dispersions are used when distilled monoglycerides are added to processed potatoes or as an aerating agent in cake emulsions.

When the lamellar dispersion is cooled below the Krafft point ( $45\text{--}50^\circ\text{C}$ ) a metastable  $\alpha$ -crystalline gel phase is formed. If the lamellar dispersion phase is acidified and cooled, the monoglycerides will transform quickly from the gel state into a  $\beta$ -crystalline coagel, which is a suspension of  $\beta$ -crystals in water,

also called a 'hydrate' in commercial terms. Such 'hydrates' are extensively used in the baking industry as crumb-softening agents in wheat bread.

The other mesophases which may be formed are the viscous isotropic, cubic phase and the hexagonal II phase described in Chapter 8.

The cubic phase is formed instantly when highly unsaturated monoglycerides from soybean oil or sunflower oil, etc. are mixed with water at room temperature (see Fig. 5.9(b)). The hexagonal II phase is formed by heating a cubic phase, or by aqueous blends of mono-, di- and tri-glycerides, like most of the commercial saturated  $35\text{--}55\%$  monoglycerides, or other complex mixtures of polar and non-polar glycerides.

Neither the cubic nor the hexagonal II phase has found a direct application, but they may be part of interfacial structures formed during processing of food emulsions.

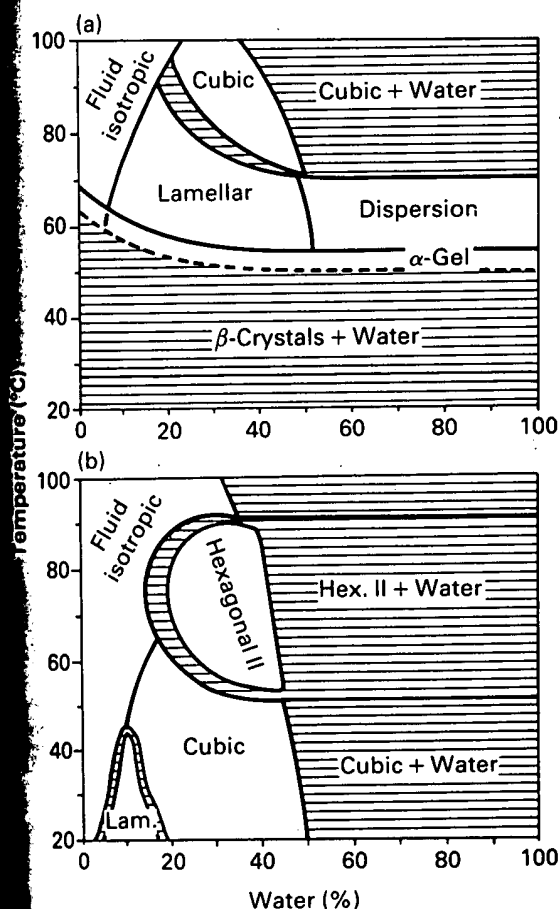


Figure 5.9 Binary phase diagrams of commercial distilled saturated monoglycerides (a) and distilled unsaturated monoglycerides (b) in water. The saturated monoglycerides are made from hydrogenated lard and contain approx. 65% monostearin and 30% monopalmitin. The unsaturated monoglycerides are made from sunflower oil and contain 21% mono-olein, 68% monolinolein and 11% saturated ( $C_{16}/C_{18}$ ) monoglycerides.

#### (b) Application in foods

Mono-diglyceride mixtures as well as distilled monoglycerides are extensively used in many industrially produced foods and often in combination with other surfactants or lecithin. Historically the first monoglycerides were applied five decades ago in the production of margarine and monoglycerides are still the emulsifier chosen to facilitate the emulsification of the water phase in the oil and fat phase of margarine. Low-calorie spreads could not be produced without surfactants such as monoglycerides.

Monoglycerides are used in ice cream to control overrun and texture. The ice cream emulsion is stabilized by the proteins present (casein and other milk proteins), and the function of monoglycerides is to control destabilization of the emulsion during the freezing process and promote flocculation of the fat globules, which is necessary to obtain optimum textural quality.

Formation of insoluble inclusion compounds with amylose—the water soluble part of starches—is another important application area for monoglycerides, especially saturated distilled monoglycerides (Krog, 1981). By complexing the amylose, monoglycerides improve texture of starch-based foods such as processed potato products, macaroni, noodles and other pasta foods.

The amylose-complexing effect is also related to the staling process of wheat bread and the baking industry therefore uses monoglycerides to impart longer shelf life to bread, rolls and buns.

Furthermore monoglycerides are used in cake shortenings to improve volume, texture and shelf life, in peanut butter to prevent oil from separating on

Table 5.6

Surfactant type	Chemical structure of main component ( $n = 10-20$ )	ADI value <sup>a</sup>	EEC No.	USFDA 21 CFR	Typical physical forms	HLB range <sup>b</sup>
Monoglycerides	$\begin{array}{c} \text{CH}_2\text{OCO}[\text{CH}_2]_n\text{CH}_3 \\   \\ \text{CHOH} \\   \\ \text{CH}_2\text{OH} \end{array}$	n.l. <sup>c</sup>	E 471	§ 182.4505 GRAS <sup>d</sup>	Powder, beads, waxy block or semi-liquid	3-4
Organic acid esters of monoglycerides: Acetic acid esters	$\begin{array}{c} \text{CH}_2\text{OCO}[\text{CH}_2]_n\text{CH}_3 \\   \\ \text{CHOH} \\   \\ \text{CH}_2\text{OCOCH}_3 \end{array}$	n.l.	E 472a	§ 172.828	Waxy block or semi- liquid	3-4
Lactic acid esters	$\begin{array}{c} \text{CH}_2\text{OCO}[\text{CH}_2]_n\text{CH}_3 \\   \\ \text{CHOH} \\   \\ \text{CH}_2\text{OCOCH}_2\text{CH}_2\text{COOH} \end{array}$	n.l.	E 472b	§ 172.852	Waxy block or flakes	3-4
Succinic acid esters	$\begin{array}{c} \text{CH}_2\text{OCO}[\text{CH}_2]_n\text{CH}_3 \\   \\ \text{CHOH} \\   \\ \text{CH}_2\text{OCOCH}_2\text{CH}_2\text{COOH} \end{array}$	—	—	§ 172.830	Waxy block or beads	5-7
Diacyl tartaric acid esters	$\begin{array}{c} \text{CH}_2\text{OCO}[\text{CH}_2]_n\text{CH}_3 \\   \\ \text{CHOH} \\   \\ \text{CH}_2\text{OCOCH}(\text{OAc})\text{CH}(\text{OAc})\text{COOH} \end{array}$	0-50	E 472e	§ 182.4101 GRAS	Powder, flakes, waxy block or semi-liquid	8-10
Citric acid esters	$\begin{array}{c} \text{CH}_2\text{OCO}[\text{CH}_2]_n\text{CH}_3 \\   \\ \text{CHOH} \\   \\ \text{CH}_2\text{OCOCH}_2\text{C}(\text{OH})(\text{CH}_2\text{COOH}) \\   \\ \text{COOH} \end{array}$	n.l.	E 472c	—	Powder, flakes	10-12
Polyglycerol esters of fatty acids $x = 1-8$	$\begin{array}{c} \text{CH}_2\text{OCO}[\text{CH}_2]_n\text{CH}_3 \\   \\ \text{CHOH} \\   \\ \text{CH}_2\text{OCOCH}(\text{O}[\text{CH}_2\text{CH}_2\text{O}]_x\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}) \end{array}$	0-25	E 475	§ 172.854	Powder, waxy block or liquid	5-13

fatty acids  $x = 1-8$

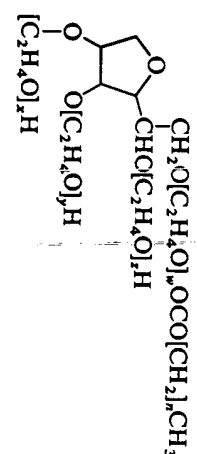


0-25 E491 \$172.842 Powder 3-6

Sorbitan esters of fatty acids



Polyoxyethylene (20) sorbitan esters (Polysorbate 60, 65, 80)  
 $x + z + y + w = 20$



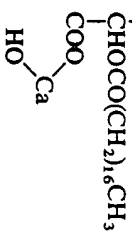
0-25 E435 \$172.836 Semi-liquid 15  
E436 \$172.838 Block 10-11  
E433 \$172.840 Liquid 15

Sodium stearyl lactylate



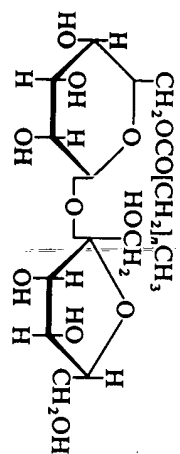
0-20 E481 \$172.846 Powder, flakes (6-8)

Calcium stearyl lactylate



0-20 E482 \$172.844 Powder, flakes 4-6

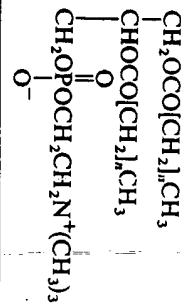
Sucrose esters of fatty acids



0-10 E473 \$172.859 Powder, beads or wax 3-15

Sucroglycerides

Lecithins (Phosphatidylcholine and other phospholipids)



0-10 E474 — —  
n.l. E322 \$182.1400 Brown, viscous fluid 6-8  
GRAS

<sup>a</sup> ADI, acceptable daily intake (mg substance per kg body weight).

<sup>b</sup> HLB, hydrophilic, lipophilic balance.

<sup>c</sup> n.l., not limited.

<sup>d</sup> GRAS, generally recognized as safe.

top of the product, in caramels and chewing gum to improve chewing properties and reduce stickiness, and in a number of other processed food items found in a modern supermarket.

## 5.8.2 Monoglyceride derivatives

Both mono-diglyceride mixtures and distilled monoglycerides are used as raw materials for making either more lipophilic or more hydrophilic derivatives which are utilized in the food industry for applications in which the monoglyceride itself does not fulfil the functional requirements.

Esters of monoglycerides with organic acids such as acetic acid, lactic acid, diacetyltartaric acid, succinic acid and citric acid are widely used as food emulsifiers. The esters are produced in standard batch reactors normally by reacting monoglycerides with the organic acid or its anhydride. A direct esterification of fatty acids, glycerol and the organic acid is also possible for some products.

### (a) Acetoglycerides

Acetylated monoglycerides, also called acetoglycerides, can be made by acetylation of distilled monoglycerides with acetic anhydride (min. 98.5% pure). The reaction takes place at a temperature of 120°C for about 1 h and acetic acid is removed by deodorization.

Acetylation may be partial or complete, depending on the ratio between acetic anhydride and monoglyceride. Normally products with 50%, 70% or 90% acetylation are used in the industry depending on application. It is also possible to make acetylated monoglycerides by interesterification of monoglycerides with triacetin.

Chemically pure acetoglycerides are polymorphic lipids. According to Martin and Lutton (1972) 1-aceto-3-stearin shows the following polymorphic transitions:  $\text{sub-}\alpha_1 \xrightarrow{3.5^\circ\text{C}} \text{sub-}\alpha_2 \xrightarrow{12.5^\circ\text{C}} \alpha \xrightarrow{45^\circ\text{C}} \beta' \xrightarrow{48.5^\circ\text{C}} \text{melt}$ . Commercially available acetoglycerides always contain small amounts of other glycerides such as mono and diglycerides, which stabilize the  $\alpha$ -crystal form obtained by cooling from melt. In practice, therefore, acetoglycerides are considered to be stable in the  $\alpha$ -crystal form ( $\alpha$ -tending).

The  $\alpha$ -crystalline state of acetoglycerides is remarkable because of its flexibility and film-forming properties. Feuge *et al.* (1952) have measured elongation of acetoglyceride samples, and found that they could be stretched eight times their original length (800%), whereas monoglyceride samples could only

be stretched to a negligible extent (4%) before breakage occurred.

Owing to their film-forming properties, acetoglycerides are used as a coating agent to act as a moisture barrier on nuts and raisins and on refrigerated meat products. Mono-acetylated acetoglycerides are also used in emulsion-type foods which are to be aerated before use, e.g. imitation creams, toppings, etc. Here they are used to improve aeration properties by promoting flocculation and destabilization of the dispersed fat globules, which are forming a structural network around the air cells in the aerated products. The degree of destabilization is an important factor for obtaining the desired quality of whipped cream. Acetoglycerides have also found an application in shortenings for cakes and icings.

### (b) Lactic acid esters

The manufacture of lactic acid esters of monoglycerides (lactylated monoglycerides) is normally based on a reaction between 88% pure lactic acid and saturated distilled, or conventional monoglycerides.

Direct esterification of glycerol, lactic acid and fatty acids is also a possible method. The lactic acid ester usually contains 15–35% esterified lactic acid. Free lactic acid and its glycerol ester are normally removed by washing with water since such water-soluble compounds can give a bitter off-taste in the finished product where the emulsifiers are used.

The structural formula for the lactylated monoglycerides shown in Table 5.6 represents the main component in the product. However, lactic acid easily forms polymers (condensation products) and, therefore, components containing di-, tri-, tetra-, etc., up to hexa-lactyl esters of monoglycerides or diglycerides are present as well. By reacting the components, glycerol – fatty acids – lactic acid, at a molar ratio of 1:1:1 the resulting product may contain a fair amount of glycerol–lactyl–fatty acid ester where the fatty acid is esterified to the OH group on the lactic acid molecule.

Lactylated monoglycerides are of the non-ionic lipophilic type of emulsifiers, completely soluble in oils and fats and only slightly water-dispersible. Like acetylated monoglycerides, they are less surface active than the corresponding monoglycerides.

Lactylated monoglyceride is stable in the  $\alpha$ -crystal form obtained on cooling from melt and is often described as an  $\alpha$ -tending emulsifier, like acetoglycerides and propylene glycol esters.

Lactylated monoglycerides are used in aerated emulsions such as toppings and imitation creams owing to their influence on fat globule destabilization analogous to acetoglycerides. Furthermore they are

used in cake mixes in combination with monoglycerides to improve cake volume and texture.

### (c) Succinic acid esters

Succinic acid esters of monoglycerides (SMG) are anionic active emulsifiers made by reacting saturated  $C_{16}/C_{18}$  fatty acid monoglycerides (preferably distilled) with pure succinic anhydride at a ratio of approximately 4:1 by weight for about 1 h at 120°C. The resulting succinic acid half ester of monoglycerides has a free carboxyl group which may be partially neutralized with alkali.

When cooled from melt to about 55°C, SMG shows a complex crystallization pattern. First it goes through a thermotropic liquid crystalline state in a temperature range from 55°C down to 48–50°C. The liquid crystalline state is characterized by having a long-range ordered structure caused by the polar group orientation, head to head, whereas the fatty acid hydrocarbon chains are still in a liquid-like state. X-ray diffraction of SMG at 50°C shows long-spacing in the order of 36–38 Å corresponding to a single chain length packing mode.

By cooling below about 48°C an  $\alpha$ -crystalline state is formed, which at room temperature transforms into a stable  $\beta$ -form with a double chain length packing as normally found in monoglycerides.

Owing to the acidity of a free carboxyl group, the SMG molecule does not swell in water. When neutralized, SMG forms lamellar mesophases in water at a temperature above 45°C. At higher water concentrations, dispersions of lamellar aggregates in equilibrium with water are formed. The lamellar phase of SMG is more stable to increased temperatures than the lamellar phase of monoglycerides and survives up to 100°C.

The application of SMG is limited to yeast-raised bakery products where it is used as a dough conditioner and crumb softener. It is often used in combination with monoglycerides in the form of aqueous hydrates ensuring good distribution in the dough system.

The function of anionic lipid surfactants as dough conditioners is not completely understood. One theory is that the surfactants react with the gluten proteins during dough mixing giving the gluten network more elasticity and strength, allowing it to expand more during fermentation and baking, yielding better volume and more uniform texture in the finished product. Another theory is based on the assumption that a dough may be regarded as a foam and that polar flour lipids as well as added surfactants stabilize the foam lamellae against coalescence. The role of surfactants in yeast dough systems is un-

doubtedly very complex, and reactions with both proteins and starch components in the aqueous phase are likely. In practical terms a dough conditioner improves handling and shock tolerance of a bread dough in automated systems making it possible to produce a satisfactory-quality product on an industrial scale.

### (d) Diacetyltartaric acid esters

Diacetyltartaric acid esters of monoglycerides (DATEM) are produced by reacting acetylated tartaric anhydride with saturated or unsaturated monoglycerides under vacuum at a temperature of 120°C for 2 h. Acetylated tartaric acid is made by reacting 3 parts of tartaric acid with 7 parts of pure acetic anhydride at 110°C for 30 min. Acetic acid is distilled off. The final step in the production of DATEM involves the reaction of diacetyltartaric anhydride with monoglycerides. Depending on the type of monoglycerides used as raw material, DATEM can be crystallized in an  $\alpha$ -like crystal form (e.g. powder or flake form) or it can be semi-liquid. DATEM does not show any polymorphism as described for SMG (Section 5.8.2c).

According to the EEC regulations DATEM may contain from 10 to 40% of esterified tartaric acid, whereas in the US the content of tartaric acid is limited to the range 14–20% by the Food Chemicals Codex.

In aqueous blends DATEM lowers the pH to about 2–3, due to its free carboxyl group. If the pH is increased to about 4–5 by neutralization with alkali, the DATEM forms lamellar mesophases which are very stable over a wide temperature range (20–80°C). In contrast to monoglycerides, DATEM is very stable in the lamellar liquid crystalline state at room temperature and shows very little tendency to form  $\alpha$ -crystalline gels, presumably owing to its bulky, polar group.

DATEMs are extensively used in yeast-raised bakery products as dough conditioners and volume enhancers, especially in European countries where rolls and buns are popular. They are specifically used in so-called bread-improver combinations which are a blend of ingredients needed in a yeast-raised dough to give a constant good-quality product even with fluctuations in the quality of the basic ingredients (flour and yeast) due to seasonal variations. The bread improver may contain surfactants such as DATEM for dough-conditioner effects, monoglycerides for crumb-softening effects, together with enzymes ( $\alpha$ -amylase), oxidizing agents (ascorbic acid) and yeast food.

DATEM is the most hydrophilic organic acid



derivative of monoglycerides. DATEM is, therefore, an effective emulsifier in oil/water emulsions such as salad dressings where it improves stability against coalescence and emulsion breakdown. It is also used as a dispersing agent for vitamin A concentrates for use in standardized milk which must contain not less than 2000 IU of vitamin A per quart.

### (e) Citric acid esters

Citric acid esters of monoglycerides (CMG) are manufactured by esterification of monoglycerides with citric acid, and the resulting product is often partially neutralized by alkali (Na salts).

Commercially available products are normally based on saturated monoglycerides with 60–90% monoglycerides, containing approximately 20% (min. 12%) esterified citric acid. The products are sold in powder or flake form.

CMG crystallizes as an  $\alpha$ -like crystal form, which is stable. It forms a milky emulsion or dispersion in water, but owing to the complex composition it forms no ordered mesomorphic structures.

Citric acid esters are used as anti-spattering agents in frying margarine. Its sodium salt is an effective oil/water emulsion stabilizer and it is used in e.g. meat emulsions, beverage emulsions etc.

### 5.8.3 Polyglycerol esters of fatty acids

Polyglycerol esters (PGE) are made by esterifying condensed glycerol with edible fatty acids using an alkaline catalyst at 230°C under vacuum. Interesterification of condensed glycerol with triglycerides is an alternative method.

The polyglycerol can have a polymerization degree from diglycerol to decaglycerol depending on the temperature (230–250°C) and time (5–7 h) of the condensation process.

According to the EEC regulations the polyglycerol moiety shall predominantly be di-, tri- and tetraglycerol, and the product must not contain more than 10% of polyglycerols equal to or higher than heptaglycerol. In the USA it is permitted to use a polymerization degree up to decaglycerol.

PGE crystallizes from the melt in an  $\alpha$ -like crystal form and does not show the polymorphism characteristic of mono-, di- or tri-glycerides. When dispersed in water above its melting point it forms a hexagonal II mesophase which on subsequent cooling forms a relatively stable  $\alpha$ -crystalline gel. The phase behaviour in water is, however, as for many

other complex mixtures of hydrophilic components, dependent on purity, degree of polymerization, fatty acid chain length and degree of unsaturation.

Polyglycerol esters have found application in various food emulsions, but their use is limited compared to monoglycerides and their derivatives. The main application of PGE is probably in cake formulations where aqueous gels of PGE are used as an aerating agent. PGE is also functional in cake shortenings for retail cakes and specific types of cake mixes. Highly polymerized polyglycerol esters can be used in beverage emulsions.

### 5.8.4 Propylene glycol esters of fatty acids

Propylene glycol esters (PGME) can be manufactured by esterifying propylene glycol with edible fatty acids using an alkaline catalyst at about 200°C under vacuum. After removal of excess propylene glycol the reaction blend may contain approximately 55% propylene glycol monoester and 45% diester. An alternative method is interesterification of triglycerides and propylene glycol yielding a reaction mixture containing the propylene glycol mono- and di-esters together with monoglycerides and minor amounts of diglycerides as well as triglycerides.

The propylene glycol monoester can be concentrated by molecular distillation. Distilled PGME contains at least 90% monoesters, and is normally based on saturated  $C_{16}/C_{18}$  fatty acids.

PGME crystallizes from melt in an  $\alpha$ -like crystal form and PGME with mixed fatty acid compositions are not polymorphic. Synthetically produced PGME based on pure fatty acids, however, does show polymorphism (Martin and Lutton, 1965), and racemic propylene glycol-1-monostearate shows four different polymorphic crystal forms, whereas optically active L(+)-propylene glycol-1-monostearate is monomorphic (Stauffer, 1967).

Propylene glycol esters belong to the so-called  $\alpha$ -tending surfactant group, like acetylated or lactylated monoglycerides. The application areas for PGME are, therefore, the same as for the two monoglyceride derivatives, i.e. in fats or shortenings for aerated food products such as cake mixes, toppings, imitation creams and icings. The functional properties of PGME are analogous to those described for acetylated and lactylated monoglycerides.

Blends of distilled PGME and distilled monoglycerides are used in aqueous gel form or in dry powder form as aerating agents in fat-free cake formulae.

### 5.8.5 Sorbitan esters of fatty acids

Sorbitan is derived from sorbitol by dehydration and then esterified with fatty acids as described for PGME. Depending on the amount of fatty acids used for esterification the equilibrium reaction mixture may contain primarily sorbitan monoesters or triesters. Sorbitan esters of palmitic or stearic acid crystallize from melt in a stable  $\alpha$ -like crystal form.

The sorbitan monostearate is frequently used in food emulsions together with more polar surfactants such as ethoxylated sorbitan esters (polysorbates) and mono-diglyceride mixtures. Typical applications are in cakes, icings, filling and coffee whitener formulations.

Sorbitan esters like sorbitan tristearate are very effective crystal modifiers in chocolate and confectionery coatings (anti-bloom agent) or in margarines formulated with fats with a tendency to form large  $\beta$ -crystals which cause textural problems (sandiness).

### 5.8.6 Polyoxyethylene (20) sorbitan esters

These very hydrophilic emulsifiers, also called polysorbates, are produced by reacting sorbitan mono fatty acid esters with 5–20 mol of ethylene oxide, and the resulting products are very complex in composition and not very well defined in structure. A possible formula is shown in Table 5.6.

During the ethoxylation process a transesterification takes place resulting in a product where the main portion of the fatty acid is esterified to the terminal ethoxylene groups instead of being esterified to the sorbitan molecule.

Polysorbates are among the most hydrophilic emulsifiers used in foods. Polysorbates form hexagonal I mesophases when dissolved in high concentrations in water. In low concentrations they form micellar solutions, and the critical micelle concentration in water at 25°C is in the order of 0.01–0.03 g/l (Becher, 1967).

In foods polysorbates are mainly used in combination with mono-diglyceride mixtures or sorbitan esters. The main areas of application are in yeast-raised bakery products (dough-conditioning effects), in cake shortenings to improve volume and texture, in icings, fillings, coffee whiteners and salad dressings, to improve emulsion stability, and in whippable emulsions, toppings, ice cream and other frozen dairy products to achieve good aeration, dryness and texture when used in combination with mono-glycerides.

### 5.8.7 Stearoyl lactylates (Na and Ca salts)

Esterification of stearic acid with lactic acid (minimum 88% pure) in the presence of sodium or calcium hydroxide (or carbonate) results in a mixture of stearoyl lactylates (sodium or calcium salts), fatty acid salts and free fatty acids. The main component is a stearoyl monolactyl ester but esters containing di-, tri- and poly-lactic acids are also present.

Sodium stearoyl lactylate (SSL) is not completely neutralized when manufactured according to the EEC or US/FDA regulations which specify an acidity of not less than 60 mg of KOH/g.

SSL crystallizes from melt in an  $\alpha$ -like crystal form which may have a single or double chain length packing mode with corresponding variations in melting points from about 45°C to 65°C.

SSL is water dispersible and forms hexagonal II mesophases at temperatures above 45°C at pH 5.0. If neutralized to pH 6.5–7.0 in water, SSL forms lamellar mesophases which can be diluted to form stable dispersions of lamellar units (Krog, 1975). Calcium stearoyl lactylate is less water dispersible, but more soluble in oils and fats than the sodium salt. Calcium stearoyl lactylate was originally developed in the USA as a dough conditioner more than two decades ago and it is still used in yeast doughs, but only to a minor extent compared to sodium stearoyl lactylate, which is one of the major dough conditioners for yeast-raised bakery products in the USA.

Sodium stearoyl lactylate is also used as an emulsifier in food emulsions such as icings, fillings, toppings and coffee whiteners. It is especially recommended for improving freeze-thaw stability of emulsions and foams.

Both sodium and calcium stearoyl lactylates are good starch-complexing agents, and are, therefore, used in processed potatoes, puddings and other starch products to reduce stickiness and improve texture. SSL also helps to extend the shelf life of bread and other bakery products.

### 5.8.8 Sucrose esters of fatty acids and sucroglycerides

Sucrose esters are manufactured by transesterification of sucrose with fatty acid methyl esters in a suitable solvent system where both components are soluble, such as dimethylformamide or dimethylsulphoxide (Benson, 1967). The sucrose esters are purified by distillation and crystallization from e.g. ethyl acetate in order to remove the solvent completely. For food use the content of dimethylformamide must be less than 1 mg/kg. An alternative

method is to react the sucrose and fatty acid methyl esters in a microemulsion using 1,2-propanediol as a solvent (Osipow and Rosenblatt, 1967).

The primary site of esterification of sucrose with fatty acid methyl esters is the sixth position on the glucose unit of the sucrose molecule. Commercial products contain, however, a mixture of sucrose mono-, di- and tri-esters.

Sucroglycerides are products made by the reaction of sucrose with triglycerides in e.g. dimethylformamide at about 140°C in the presence of an alkaline catalyst. The sucroglycerides contain a mixture of 40–60% sucrose esters, the balance being mono-, di- and tri-glycerides.

Sucrose esters of palmitic and stearic acids, which are the most common types available, are solid at room temperature. They crystallize in a stable  $\alpha$ -like crystal modification.

Sucrose esters with high HLB (hydrophil, lipophil balance) numbers are water-soluble and form lamellar mesophases in concentrated bulk solutions. In aqueous solutions and emulsions they have properties similar to polysorbates.

Sucroglycerides generally show the same properties as corresponding sucroesters, but the glycerides present may interfere with the functional properties.

Sucrose esters are functional surfactants in food emulsions like margarine, ice cream, toppings and cake emulsions. They have also shown dough-conditioning and crumb-softening effects in bread (Breyer and Walker, 1983). Except in Japan, where they are generally accepted, sucrose esters are not yet widely used in foods. Recently, the US/FDA has approved the use of sucrose esters in baked goods and dairy products (Federal Register, 1983).

### 5.8.9 Lecithins (phosphatidylcholines)

The production of lecithin from soybeans is described in Section 5.4. Lecithin is the commercial name given to a mixture of phospholipids, naturally occurring in animal or vegetable products such as egg yolk (8–10% phospholipids), butter (0.5–1.2%), wheat lipids (approx. 0.5%) soybean (1.5–3%) and other oil seeds. More details on the chemical composition and physical properties of lecithin appear in Sections 2.3, 3.11, 6.3, 8.10 and 11.2.

Lecithin is a natural surfactant and has been used as an emulsifier in foods since the last century. The first application of egg lecithin in an industrial food product was in margarine in 1896. In 1922 soybean lecithin became commercially available and it is still extensively used in margarine together with monoglycerides. Lecithin from egg yolk is the primary emulsifier in mayonnaise.

Lecithins are used in a great variety of processed foods such as bread, cakes and biscuits, chocolate, sugar confectionery products, cocoa powder, coffee whiteners, dried milk products and baby foods.

### 5.8.10 Non-food applications

Lipid surfactants are used as emulsifiers, texturizing agents, lubricants and plasticizers in pharmaceuticals, cosmetics, textiles, extended plastics and oil drilling fluids etc.

Polysorbates and sorbitan esters are used in pharmaceutical emulsions or dispersions containing vitamins or hormones. Lipophilic surfactants such as monoglycerides, propylene glycol ester or sorbitan esters are used as suppository bases. Monoglycerides and other lipophilic surfactants are typical compounds in cosmetic water/oil or oil/water creams, lotions and gels. Hydrophilic surfactants are used to solubilize perfume oils in various cosmetic oils and lotions.

The plastics industry uses surfactants as lubricants in processing (extrusion) of plastic products made from polyvinyl chloride, polystyrene etc., or as anti-statics and anti-fogging agents in polyolefins (films). Monoglycerides are also used as fabric softeners in laundry detergents.

### 5.8.11 Legal aspects

Before a new type of food surfactant is permitted for use by the health authorities it has to be tested in a number of toxicological studies including short-term and long-term feeding trials on several species together with studies on metabolism. (WHO, 1974).

The FAO/WHO Joint Expert Committee on Food Additives has established acceptable daily intake (ADI) values for surfactants (Table 5.6) and these values are used as a guidance by health authorities in the various countries where food laws exist.

Surfactants for which ADI values are not specified are often permitted for use in foods without limiting the use level provided that it does not exceed good manufacturing practice. For surfactants with limited ADI values the permitted maximum use level in various foods is calculated on the basis of the current eating habits in the individual countries of the world.

The EEC Council Directive of 18th June 1974, 74/329/EEC with later amendments lists permitted surfactants which are assigned an E number and such surfactants may be authorized for use in food by all member states of the EEC.

In the USA surfactants are regulated by the US Food and Drug Administration, Washington D.C.

Surfactants that are generally recognized as safe (GRAS) by US/FDA when used in accordance with good manufacturing practice can be used within practical and needed limits. Surfactants that are not GRAS substances are regulated in use level in specified food products according to the specifications given for each regulated surfactant in the Central Federal Register, Title 21.

Surfactants which have been approved for use in food by the EEC or the US/FDA regulation should be regarded as safe food ingredients, when used as prescribed by the health authorities.

## References

- Becher, P. (1967) *Nonionic Surfactants* (ed. M.J. Schick), Marcel Dekker, New York, p. 481.
- Benson, F.R. (1967) *Nonionic Surfactants* (ed. M.J. Schick), Marcel Dekker, New York, p. 247.
- Breyer, L.M. and Walker, C.E. (1983) *J. Food Sci.*, **48**, 955.
- Federal Register (1983) **48**, No. 164, 38225-38227.
- Feuge, R.O., Vieknolr, E.J. and Loogren, N.V. (1952) *J. Amer. Oil Chem. Soc.*, **29**, 11.
- Krog, N. (1975) *Water Relations of Foods* (ed. R.B. Duckworth), Academic Press, London, p. 587.
- Krog, N. (1981) *Cereal Chem.* **58**, 158.
- Krog, N. and Birk Lauridsen, J. (1976) *Food Emulsions* (ed. S. Friberg) Marcel Dekker, New York, p. 67.
- Krog, N. and Borup, A.P. (1973) *J. Sci. Food Agric.*, **24**, 691.
- Martin, J.B. and Lutton, E.S. (1965) *J. Amer. Oil Chem. Soc.*, **42**, 529.
- Martin, J.B. and Lutton, E.S. (1972) *J. Amer. Oil Chem. Soc.*, **49**, 683.
- Osipow, L.I. and Rosenblatt, W. (1967) *J. Amer. Oil Chem. Soc.*, **44**, 307.
- Søe, J.B. (1983) *Fette Seifen Anstrichm.*, **85**, 72.
- Sonntag, N.O.V. (1982) *Bailey's Industrial Oil and Fat Products*, (ed. D. Swern) John Wiley & Sons, New York, Vol. 2, p. 97.
- Stauffer, C.E. (1967) *J. Amer. Oil Chem. Soc.*, **44**, 443.
- WHO (1974) *Food Additives Series No. 5*, World Health Organization, Geneva, p. 7.

orthorhombic  $O1$ , and the angle of tilt of the chains towards the end group plane is  $62^\circ$ . A second  $\beta'$ -form ( $\beta_1$ ), which is closely related in structure according to the X-ray diffraction data can be obtained from the melt or by rapid crystallization from solvents.

The methyl esters of fatty acids with an odd number of carbon atoms in the chain crystallize from the melt in an  $\alpha$ -form with a large stability interval. In this respect the odd esters are similar to normal paraffins where odd numbers give a stable  $\alpha$ -form over a broad temperature range.

Ethyl stearate separates from the melt as an  $\alpha$ -form with the characteristic transparent and plastic

character due to the rotational disorder. At lower temperature this form is transformed into a  $\beta'$ -form (originally termed  $\beta$  on the basis of its highest melting point). This  $\beta'$ -form can also be obtained from solvents. The crystal structure has been determined (Aleby, 1968). In this ester, as well as in esters of longer alcohols, all molecules have the same direction, with the alcohol groups of one molecular layer facing the end groups of the fatty acid chain in the adjacent layer (head-to-tail). Such an arrangement should be expected, as the polar forces between the carboxyl groups must be very weak at these long distances (the molecules have to be extended for space-filling reasons).

### 8.5.2 Melting point and heat of fusion

The melting of longer homologues of saturated fatty acids takes place as  $C \rightarrow \text{liq.}$  in even numbers and  $C' \rightarrow \text{liq.}$  in odd ones. The melting points are given in Table 8.2. There is a pronounced alternation between even and odd members; the even members show a melting curve at a somewhat higher temperature than the curve formed by odd acids. The alternation of melting points can be explained by the methyl end group structure (Larsson, 1966). The crystal structures of the form C and C' are isomorphous, which means that the difference is only due to packing differences over the methyl end group gap in the two forms. A denser packing is achieved when the last bond in the chain ( $\text{CH}_2\text{--CH}_3$ ) is almost perpendicular to the end group plane, and this is the case in the C-form of even fatty acids.

The melting point curves show a convergence behaviour towards an asymptotic value of about  $120\text{--}125^\circ\text{C}$  for infinitely long chains.

A few of the naturally occurring unsaturated fatty acids are also shown in Table 8.2. Depending upon the position of the double bond there is a well-known reduction in the melting point compared to the corresponding saturated fatty acids. This temperature reduction in a  $\text{C}_{18}$  chain with one double bond is only a few degrees when the double bond is near the carboxyl group ( $\Delta 2\text{--}\Delta 5$ ), whereas it increases successively towards the methyl end to about  $50^\circ\text{C}$  at the position  $\Delta 12$ . The reduction in melting point by a *trans* double bond is much smaller, but otherwise it follows the same behaviour as *cis* double bonds. A *trans* double bond in position  $\Delta 10\text{--}\Delta 12$  causes a reduction in melting point of about  $20^\circ\text{C}$  compared with the corresponding saturated chain (m.p. of stearic acid  $69.6^\circ\text{C}$  and of elaidic acid  $43.7^\circ\text{C}$ ).

The heat of fusion of the even-membered saturated long-chain fatty acids involves the C-form according

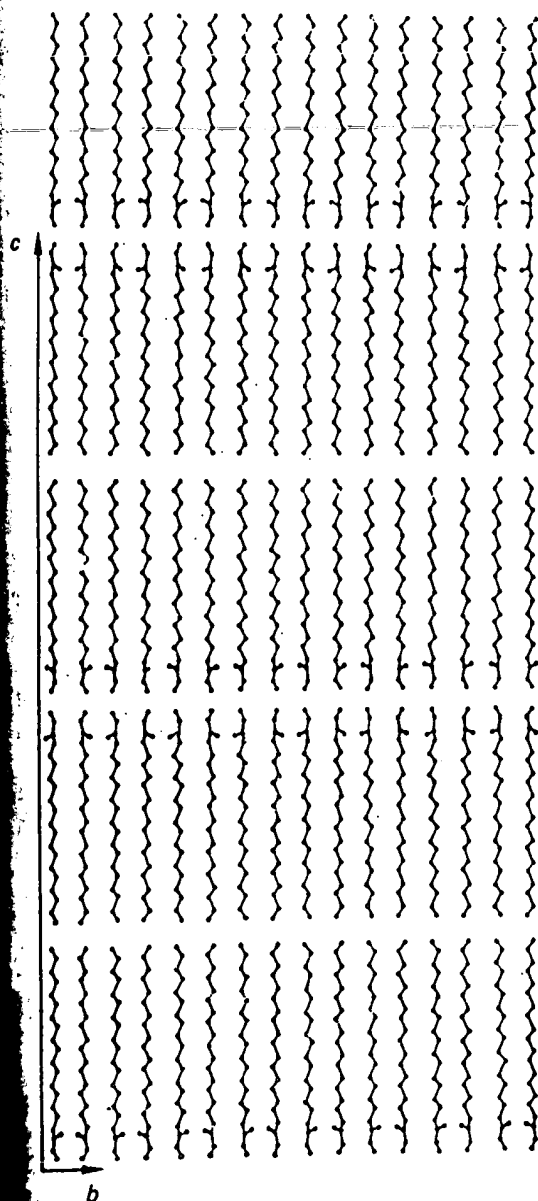


Figure 8.36 A projection of the crystal structure of methyl stearate viewed along the shortest unit cell axis (Aleby and von Sydow, 1960).

## Structural and physical characteristics

**Table 8.2** Melting points of fatty acids according to Bailey (1950). Values given by Fasman (1975), when different, are shown afterwards within parentheses

Fatty acid		m.p. (°C)
Butanoic	4:0	-7.9
Pentanoic	5:0	-34.5
Hexanoic	6:0	-3.4
Heptanoic	7:0	solid. p. -7.5 (-10.5)
Octanoic	8:0	16.7
Nonanoic	9:0	12.5
Decanoic	10:0	31.6
Undecanoic	11:0	29.3
Dodecanoic	12:0	44.2
Tridecanoic	13:0	41.5
Tetradecanoic	14:0	54.4 (53.9)
Pentadecanoic	15:0	52.3
Hexadecanoic	16:0	62.9 (63.1)
Heptadecanoic	17:0	61.3
Octadecanoic	18:0	69.6
Nonadecanoic	19:0	68.65 (68.6)
Icosanoic	20:0	75.35 (76.5)
Henicosanoic	21:0	74.3
Docosanoic	22:0	79.95 (81.5)
Tricosanoic	23:0	79.1
Tetracosanoic	24:0	84.15 (86.0)
Pentacosanoic	25:0	83.5
Hexacosanoic	26:0	87.7 (88.5)
<i>cis</i> -unsaturated		
Palmitoleic	16:1	0.5
Oleic	18:1	16.25 and 13.36
Gadoleic	20:1	25
Erucic	22:1	33.4
Linoleic	18:2	-5.0
Linolenic	18:3	-11.0
Arachidonic	20:4	-49.5

to the polymorphic behaviour discussed above. The value in stearic acid (Singleton *et al.*, 1950), for example, is  $\Delta H_f = 16.36 \text{ kcal mol}^{-1}$ . Above  $C_{10}$  in chain length the end group contribution to the heat of fusion remains constant, so there is a regular increase with the number of  $\text{CH}_2$  groups according to the formula:

$$\Delta H_f = (n - 2)a + b$$

with  $a$  and  $b$  equal to 1.03 and -1.55 for even fatty acids, and 0.97 and -2.50 for odd fatty acids respectively (Bailey, 1950). The expression  $(n - 2)$ , with  $n$  equal to the number of carbon atoms, is equal to the number of  $\text{CH}_2$  groups in a saturated chain. A statistical mechanical theory of melting has been reported by Aggarwal and Bhatnagar (1972), and calculated values of the heat of fusion are in fair agreement with experimental data.

Finally some thermal data for the different polymorphic forms of esters will be given.

**Table 8.3** Melting point of the  $\beta'$ -form of different esters (Malkin, 1936)

	Palmitate	Stearate
Methyl	—	38.8
Ethyl	23.5	30.5
n-Propyl	20.4	30.5
n-Butyl	16.9	27.5
n-Amyl	19.4	30
n-Octyl	22.5	31.8
n-Hexadecyl	51.6	56.6

(a) *Methyl esters*: Two crystal forms with close melting points can be obtained from the melt. Their melting points are 28.95 °C and 29.20 °C in methyl palmitate, 37.37 °C and 37.80 °C in methyl stearate and 51.65 °C and 51.84° in ethyl behenate (Francis and Piper, 1939).

(b) *Ethyl esters*: The  $\alpha$ -form is obtained by cooling to 19.8 °C, 30.75 °C and 40.5 °C for ethyl palmitate, ethyl stearate and ethyl icosanoate respectively. The  $\alpha$ -form is transformed into the stable crystal form, which (according to the nomenclature in Section 8.1) is a  $\beta'$ -form. The melting points of these esters are 25 °C, 34 °C and 41 °C respectively (Malkin, 1933).

(c) *Higher esters*: Melting points of a series of esters of palmitic and stearic acid are given in Table 8.3. The  $\alpha$ -form, obtained from the melt, is transformed to a  $\beta'$ -form. It can be seen that there is a minimum in the melting points at the butyl ester of both series.

### 8.5.3 Vapour pressure, boiling point and heat of vaporization

Values for the vapour pressure of the most important fatty acids are given in Table 8.4 and of some esters in Table 8.5. Boiling points are listed in Table 8.6.

The temperature dependence of the vapour pressure is related to the enthalpy of sublimation ( $\Delta H_s$ ) of the crystals by the Clapeyron equation:

$$dP/dT = \Delta H_s/T(V_g - V_c)$$

where  $V_g$  and  $V_c$  are the molal volume of the vapour and the crystal respectively. The enthalpy of sublimation can also be obtained from the enthalpy of fusion and the enthalpy of vaporization ( $\Delta H_s = \Delta H_f + \Delta H_{vap}$ ) provided that these enthalpies are determined at the same temperature. The enthalpy of sublimation is very interesting from a theoretical point of view as it is equal to the lattice energy of the crystal structure (if the vapour phase behaves ideally). Selected values of heats of sublimation and heats of vaporization are given in Tables 8.7-8.9.

Table 8.4 Boiling points of fatty acids at pressures between 1 and 760 mmHg (Jordan, 1954)

Pressure (mmHg)	Temperature (°C)				
	Dodecanoic	Tetradecanoic	Hexadecanoic	Octadecanoic	Oleic
1	121.0	142.0	153.6	173.7	176.5
5	150.6	174.1	188.1	209.0	208.5
10	166.0	190.8	205.8	225.0	223.0
20	183.6	207.6	223.8	243.4	240.0
40	201.4	223.5	244.4	263.3	257.2
60	212.7	237.2	256.0	275.5	269.8
100	227.5	250.5	271.5	291.0	286.0
200	249.8	272.3	298.7	316.5	309.8
400	273.8	294.6	329.0	343.0	334.7
760	299.2	318.0	353.8	370.0	360.0

Table 8.5 Boiling points of some fatty acid methyl esters at pressures between 1 and 20 mmHg (Jordan, 1954)

Pressure (mmHg)	Temperature (°C)		
	Palmitate	Stearate	Oleate
1	134.3	—	—
2	—	166	166.2
4	—	181	182
5	166.8	—	—
6	—	191	192
8	—	199	199.5
10	184.3	204	205.3
20	202.0	—	—

Table 8.6 Boiling points of fatty acids (Singleton, 1960)

Fatty acid	Boiling point (°C/mmHg)
Methanoic	100.5
Ethanoic	118.2
Propanoic	141.1
Butanoic	163.5
Pentanoic	187
Hexanoic	205.8
Heptanoic	223.0
Octanoic	239.7
Nonanoic	255.6
Decanoic	270
Undecanoic	284
Dodecanoic	225/100
Tridecanoic	236/100
Tetradecanoic	250/100
Pentadecanoic	202.5/10
Hexadecanoic	268/10
Heptadecanoic	220/10
Octadecanoic	213/5
<i>cis</i> -9-Octadecenoic (Oleic)	234/15
<i>trans</i> -9-Octadecenoic (elaidic)	288/100
<i>cis</i> -9, <i>cis</i> -12-Octadecadienoic (linoleic)	202/1.4

Table 8.7 Calculated values of heat of vaporization of some fatty acids at various temperatures, after Singleton (1960)

Fatty acid	Temperature (°C)	$\Delta H_{\text{vap}}$ (cal g <sup>-1</sup> )
Lauric	164	97
	243	77
Myristic	182	93
	209	87
Palmitic	243	75
	202	84
Stearic	244	76
	242	67

Table 8.8 Heat of vaporization of some short-chain esters (Svensson, 1980)

	$\Delta H_{\text{vap}}$ (kJ mol <sup>-1</sup> )
Methyl ethanoate	32.60 ± 0.06
Methyl propanoate	35.82 ± 0.09
Methyl butanoate	39.28 ± 0.22

**Table 8.9** Heat of sublimation of fatty acids (Davies and Malpass, 1961)

Fatty acid	$\Delta H_s$ (kcal mol <sup>-1</sup> )	Temperature range (K)
Decanoic acid	28.0	290–301
Dodecanoic acid	33.5	296–314
Tetradecanoic acid	33.4	312–325
Hexadecanoic acid	36.9	320–333
Octadecanoic acid	39.8	331–340
Icosanoic acid	47.7	337–346
Docosanoic acid	46.2	345–352

#### 8.5.4 Density and specific volume

Dilatometric methods are frequently used in studies of phase transitions in lipids as the dilatometric curves are very informative in that respect. Such a dilatometric curve is obtained by plotting specific volume versus temperature. It has been found that the ratio between specific heat and the coefficient of expansion is nearly constant at different temperatures. This can be a useful relationship. If, for example, complete data on specific heats are available a single determination of the coefficient of expansion can be used for estimation of the specific volume over a wide temperature range.

The density of the B-form of stearic acid from flotation measurements was found to be 1.036 g cm<sup>-3</sup>, and the calculated density from unit cell dimensions was 1.041 ± 0.005 g cm<sup>-3</sup> (von Sydow, 1955). Calculation of the density changes of this B-form according to unit cell data between 0 °C and the transition point near 45 °C shows very small density differences, from 1.0444 to 1.0349 g cm<sup>-3</sup> (Degerman and von Sydow, 1959). The C-form of stearic acid shows much stronger density variations with temperature. Thus between 0 °C and the melting point, near 70 °C, the calculated density changes from 1.0293 to 0.9995 (Degerman and von Sydow, 1959). The C-form has obviously a much more flexible structure which can allow a higher degree of thermal mobility of the chains. The density for the A-form, although the least-stable form, is close to those of the B- and C-forms. The density according to flotation for the A'-form of pentadecanoic acid was found to be 1.02 g cm<sup>-3</sup> and the calculated density from unit cell dimensions was 1.034 ± 0.016 g cm<sup>-3</sup> (von Sydow, 1954).

The density for branched-chain fatty acids is considerably lower than that of the corresponding n-fatty acid. A methyl branch at different positions along a C<sub>18</sub> chain gives small variations in density as shown in Table 8.10.

**Table 8.10** Density of branched-chain fatty acids (Abramsson, 1956, 1958, 1959a)

Branched octadecanoic acid	Density observed (g cm <sup>-3</sup> )	Density calculated
2-D-Methyl	1.015	1.015 ± 0.010
2-DL-Methyl	0.998	1.001 ± 0.010
9-DL-Methyl	0.998	0.991 ± 0.010
14-DL-Methyl	0.94	0.95 ± 0.02
16-DL-Methyl	0.998	1.001 ± 0.010

#### 8.5.5 Viscosity

Dynamic viscosity measurements have been reported (Fernandez-Martin and Montes, 1976) for the saturated fatty acids C<sub>12</sub>–C<sub>18</sub> between 70 and 90 °C. A Newtonian behaviour was obtained at all shear rates with the values of  $\eta$  (cP) at 70 and 90 °C respectively:

C <sub>12</sub>	4.415	2.982
C <sub>14</sub>	5.984	3.906
C <sub>16</sub>	7.682	4.885
C <sub>18</sub>	9.583	6.294

Many binary, ternary and quaternary mixtures of these acids were also examined and it was found that the viscosity of these mixtures fall on the same line as that of the components, provided that an average chain length is defined

$$n = \sum x_i n_i$$

where  $x_i$  is the molar fraction and  $n_i$  the number of carbon atoms of the  $i$ th component. The lines of the experimental values were fitted by regression methods and the regression parameters obtained for the data at 70 °C were:

$$\log \eta = -0.602802 + 0.134844\bar{n} - 0.002591(\bar{n})^2$$

The data of the multicomponent mixtures were thus in agreement with the 'principle of congruence' introduced by Bröndsted and Kofoed (1946).

Using a rotational-torsional surface viscosimeter, the surface shear viscosity of the C<sub>15</sub>–C<sub>20</sub> straight-chain fatty acids have been determined (Moo-Young *et al.*, 1981). The even fatty acids were found to show a surface-Newtonian behaviour, with  $\eta_s$ -values of 1.5, 2 and 3 mN s/m for the C<sub>16</sub>, C<sub>18</sub> and C<sub>20</sub> members respectively. The odd acids, however, showed a surface-pseudoplastic behaviour. Thus C<sub>17</sub> gave decreasing surface shear viscosity up to a sharp rate of 8 s<sup>-1</sup>, and beyond that value the viscosity remained constant at about 0.6 mN s/m. These data indicate different monolayer structures of the even and odd members.



Viscosity data on fatty acids in the liquid state at various temperatures in solutions can be found in a review by Singleton (1960).

### 8.5.6 Refractive index

The ratio of the speed of electromagnetic radiation in vacuum to that in a particular medium is known as the absolute index of refraction of the medium,  $n$ :

$$n = c/v$$

According to Maxwell's relation,

$$n = \sqrt{K_e}$$

where  $K_e$  is the static dielectric constant. This relation is, however, true only for simple gases. The interaction between the applied electric field and the molecules of the medium results in additional field components. The refractive index depends on the frequency of the radiation which is known already from Isaac Newton (dispersion of white light by glass prisms).

Values of the refractive index for various fatty acids are given in Table 8.11.

Table 8.11 Refractive indices of some fatty acids and their methyl esters, from Singleton (1960)

Substance	Refractive index at temp. $t(^{\circ}\text{C})$
	$n_D^{85.6}$
Palmitic acid	1.42545
Stearic acid	1.42830
Arachidic acid	1.43066
Behenic acid	1.43257
	$n_D^{35}$
Oleic acid	1.45442
Icosenoic acid	1.45574
Erucic acid	1.45674
	$n_D^{60.2}$
Methyl palmitate	1.42549
Methyl stearate	1.42897
Methyl arachidate	1.43165
Methyl behenate	1.43391

### 8.5.7 Solubility

Ideal solubilities, derived from the Clausius-Clapeyron equation, can be expressed by the equation:

$$2.3 \log X = \frac{\Delta H_F}{R} \left( \frac{1}{T_F} - \frac{1}{T} \right)$$

where  $X$  is the mol fraction of the solute,  $\Delta H_F$  is the heat of fusion of the solute and  $T_F$  is the melting point of the solute (K).

The solubilities of fatty acids, although deviating from ideal behaviour, are known to vary regularly with molecular weight according to the formula:

$$\log S = c + kM$$

where  $S$  is the solubility in mol %, thus:

$$S = \frac{\text{moles dissolved}}{\text{moles solvent} + \text{moles dissolved}} \times 100$$

Using the early data of fatty acid solubility in water from Ralston *et al.* (1942) the values  $c = 0.0176$  and  $k = -0.0173$  are obtained for the  $C_{10}$ – $C_{18}$  saturated fatty acids. Even and odd fatty acids follow the same curve, i.e. no alternation. If the solubility of the same fatty acids in benzene is compared, however, they alternate (Brensch and Kirkali, 1968). Thus the  $C_{12}$ – $C_{18}$  even members follow a line with  $k = -0.0261$  and  $c = 0.2696$ , whereas the  $C_{13}$ – $C_{17}$  odd members give values of  $k = -0.0250$  and  $c = 6.4761$ . A probable explanation for this difference in alternation is the difference in methyl end group structure. Different end group structure in even and odd members means that there is a difference in surface energy (see also Section 8.5.2). A solvent like benzene has a surface energy close to that of the methyl end group surface of the crystals, whereas water has a far higher value. Thus the interfacial energy at the water/crystal surface interface is so high that the variations in surface energy between even and odd members can be neglected, contrary to the situation at the benzene/crystal surface interface.

The solubility in water will first be considered. Accurate values are difficult to determine, due to strong variations with pH, and it is therefore necessary to take into account the amount of carbon dioxide dissolved in the water. Bell (1973) has published a critical analysis of the solubility in water. Instead of the molecular weight, given in the formula above, he has used the number of carbon atoms in the chain ( $n$ ), i.e.:

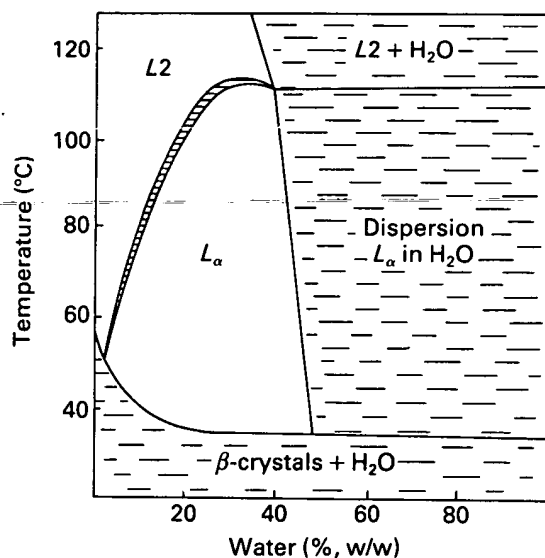
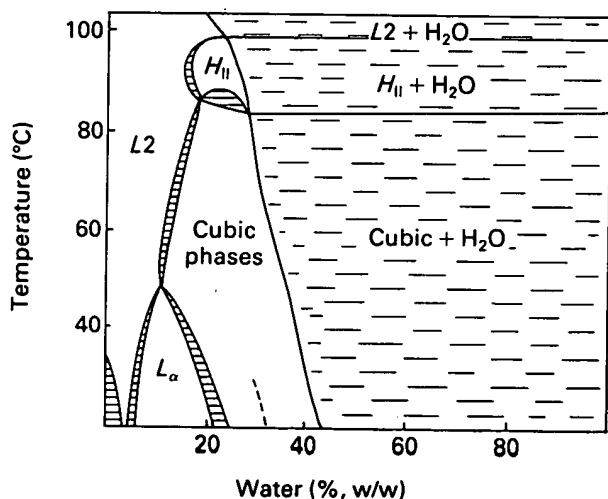
$$\log S = c + kn$$

The most reliable data for fatty acids were found to obey a value of  $c = 2.32$  and  $k = -0.60$ . The corresponding values for  $n$ -alcohols are rather close, with  $c = 2.3$  and  $k = -0.58$ . The scattered values of the fatty acid dissociation constants are also considered in the paper by Bell. It is concluded that at  $C_{10}$  and above this chain length, the dissociation constant is  $1.20 \times 10^{-5}$  mol/l.

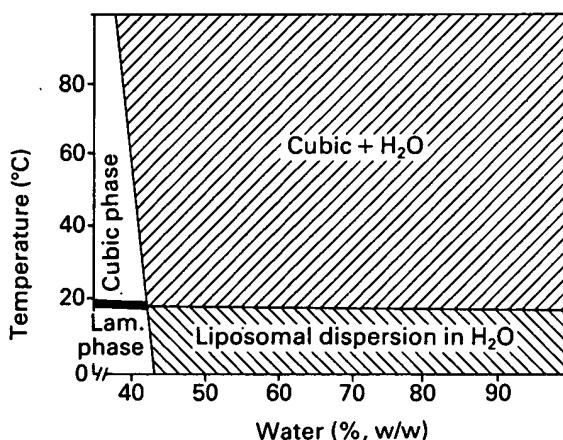
There is one additional difficulty in the determination of water solubility of lipids, which often is neglected. The surface activity of lipid molecules

**Table 8.20** Melting point and  $\alpha \rightleftharpoons$  sub- $\alpha$  transition of saturated mono-glycerides according to Malkin (1954)

Glycerol 1-alkanoate	$\beta$ (°C)	$\beta'$	$\alpha$	$\alpha \rightarrow$ sub- $\alpha$
Decanoate	53	49	27	8
Undecanoate	56.5	52	36.5	3
Dodecanoate	63	59.5	44	15
Tridecanoate	65	61	50	9
Tetradecanoate	70.5	67.5	56	24
Pentadecanoate	72	69	62	17
Hexadecanoate	77	74	66.5	34
Heptadecanoate	77	74.5	70	28
Octadecanoate	81.5	79	74	47

**Figure 8.45** Phase diagram of the binary system mono-laurin-water.**Figure 8.46** Phase diagram according to Lutten (1966) and Krog *et al.* (1984) of mono-olein-water. The broken line indicates the transition between the two cubic phases at low temperatures.**Table 8.21** Melting and solidification points of 2-mono-glycerides according to Malkin (1954)

Glycerol 2-alkanoate	m.p. (°C)	s.p.
Decanoate	40.2	34.0
Dodecanoate	51.0	47.5
Tetradecanoate	61.3	58.0
Hexadecanoate	69.0	65.5
Octadecanoate	75.2	70.0

**Figure 8.47** Main features of the phase diagram 2-mono-olein-water (Ljusberg-Wahren *et al.*, 1983).

diagrams given for monolaurin and monoerucin contain some errors. A revised phase diagram of monolaurin is given in Fig. 8.45; the revised phase diagram of monoerucin has been published earlier (Larsson *et al.*, 1978).

The phase diagram of mono-olein is given in Fig. 8.46, where the occurrence of the two cubic phases (see Section 8.2) is indicated. It is also of interest to compare this phase diagram with that of 2-mono-olein indicated in Fig. 8.47. All monoglycerides of the aqueous systems discussed above consist of an equilibrium mixture of about 90% (w/w) of the 1-isomer and 10% of the 2-isomer owing to the rapid

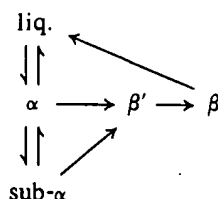
## 8.7 Monoglycerides (monoacylglycerols)

### 8.7.1 Solid state behaviour

*2-Monoglycerides* have a quite simple phase behaviour. When the melt is cooled, a thermotropic liquid-crystalline phase is first formed (at 47 °C in 2-monolaurin). A monotropic transition into the  $\beta$ -form (at 40 °C in 2-monolaurin) then takes place. There is only one crystal form in the solid state, which is unusual in lipids. The crystal structure of 2-monolaurin (Larsson, 1964a) is shown in Fig. 8.43. The hydrogen-bond system, where only hydroxyl groups are involved, links the molecules both laterally and over the gap between the two halves of the bilayer. The chains are packed according to the triclinic chain packing  $T_{||}$ , and tilted 44° towards the end group plane.

The reason why a liquid-crystalline phase and no  $\alpha$ -form is obtained, when the melt is cooled, is probably related to the bulky polar head-group. The cross-section area per molecule in the plane of the bilayer in the  $\beta$ -crystal form (Fig. 8.43) is in fact very close to that in the lamellar liquid-crystalline phase (see Section 8.2).

*1-Monoglycerides* show a rather complex phase behaviour contrary to the 2-isomer. A study of the racemic saturated monoglycerides (Larsson, 1964b) shows the following transition scheme:



An  $\alpha$ -form separates from the melt which is transformed reversibly into a sub- $\alpha$  form (a  $\beta$ -form) at about 25 °C lower temperature. Alternatively the  $\alpha$ -form is transformed irreversibly into a  $\beta'$ -form. There are furthermore two  $\beta$ -forms, but they are so closely related in structure (the same bilayer units) that only one form is indicated in the scheme above. The  $\beta'$ - and  $\beta$ -forms can also be crystallized from solvents.

A remarkable feature in these polymorphic changes is that the bilayer layer thickness is constant in all crystal forms which illustrates the dominating effect of the structure in the polar region. The chain packing in the  $\beta$ -forms is the monoclinic  $M_{||}$  and these crystal forms are truly racemic. The  $\beta'$ -form, however, is isomorphous with the  $\beta'$ -form of optically active 1-monoglycerides, so obviously the two antipodes separate into different D- and L- $\beta'$

crystals. This appears to be the main difference between the sub- $\alpha$  and the  $\beta'$ -form which both have the same angle of tilt and the same chain packing ( $O_{||}$ ).

The crystal structure of the L-1-monoglyceride of 11-bromoundecanoic acid is shown in Fig. 8.44. As in the 2-monoglyceride  $\beta$ -form only the hydroxyl groups participate in the hydrogen-bond system which seems to be a general feature in monoglyceride crystal forms.

### 8.7.2 Melting points and transition temperatures

The thermal transition point of the different polymorphic forms of saturated *1-monoglycerides* have been reported by Malkin (1954), and selected values are given in Table 8.20 (using the nomenclature defined in Section 8.1). The values are in close agreement with the data reported by Lutton and Jackson (1948).

*2-Monoglycerides* have also been examined by Malkin (1954) and the melting and solidification points of saturated members are given in Table 8.21. It should be pointed out that in the gap between the reported melting point and the solidification point a thermotropic liquid-crystalline phase is formed as described above.

The melting point of the most stable forms of 1-mono-olein and 1-monoelaidin, which are  $\beta$ -forms, are 35.0 °C and 58.5 °C respectively. When 1-mono-olein solidifies from the melt, a thermotropic liquid-crystalline phase with lamellar structure is formed as a metastable transition state.

### 8.7.3 Interaction between monoglycerides and water

Phase diagrams of monoglyceride-water systems have been reported by Lutton (1966) ( $C_{12}$ - $C_{22}$ ), Larsson (1967) ( $C_6$ - $C_{10}$ ) and Krog and Larsson (1968) (industrially distilled monoglycerides). The main features of the different monoglyceride-water systems were given in Section 8.2 as an illustration of lipid-water phase equilibria (Fig. 8.12). Only additional comments to this earlier work will be given here.

The phase described by Lutton (1966) as a middle phase, which is the term used in soap-water systems for the hexagonal phase  $H_1$ , is in fact the inverse structure; i.e. phase  $H_{II}$ . Furthermore the phase